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13. ABSTRACT

With the help of the support we have received from the United States Advanced Research Projects Agency through the United States Army our laboratory has pioneered lensless near-field optics. The optical resolution that has been achieved with this novel advance has already carried optics to a new frontier of resolution in the range of tens of nanometers. These studies have indicated that the ultimate resolution that could be achieved with this new direction in optics could even approach the dimension of a single atom or molecule. Thus, the barrier of optical resolution has been broken by the revolution that has occured as a result of the development of near-field optical imaging.

Near-field optics elegantly bridges both exciting fundamental research and a wide variety of practical applications. These applications portend a relatively transparent integration of near-field optical technology with currently available far-field optical techniques to overcome the solid brick wall of resolution that many of these optical applications now experience.

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"Development Novel Subwavelength Light sources and Lasers."

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With the help of the support we have received from the United States Advanced Research Projects Agency through the United States Army our laboratory has pioneered lensless near-field optics. The optical resolution that has been achieved with this novel advance has already carried optics to a new frontier of resolution in the range of tens of nanometers. These studies have indicated that the ultimate resolution that could be achieved with this new direction in optics could even approach the dimension of a single atom or molecule. Thus, the barrier of optical resolution has been broken by the revolution that has occured as a result of the development of near-field optical imaging.

Near-field optics elegantly bridges both exciting fundamental research and a wide variety of practical applications. These applications portend a relatively transparent integration of near-field optical technology with currently available far-field optical techniques to overcome the solid brick wall of resolution that many of these optical applications now experience.

What is Near-Field Optics?

Near-field optics is the development of optical elements that can work in the near-field of an object that is to be interogated by light. In essence, the objective is to develop optical elements that can illuminate, detect and/or enhance optical phenomena within a distance, from the object, that is considerably less than the dimensions of one wavelength. Conventional optical instruments all of which work in the far-field are based on lenses which critically depend on the wave nature of light. Thus, these elements are inherently limited to operation in the far-field with associated problems of diffraction that intrinsically limits resolution to approximately half the wavelength of light. Near-field optical elements not only overcome this diffraction limit of resolution but also relax the wavelength dependence of optical resolution.

In its simplest implementation [1] near-field optics involves transmitting light through a subwavelength aperture that is brought in close proximity to a surface. The sample or the aperture is then scanned in order to obtain an image or create a pattern with the subwavelength spot of light that emanates from this near-field optical element. The rule of thumb appears to be that the near-field extends for a dimension that is comparable to the aperture diameter that is being employed. Calculations indicate that light emanating from a subwavelength aperture is initially confined to the diameter of the aperture and has, in the near-field, an exponentially decreasing intensity distribution as the beam spreads out from the surface of the aperture.

During the past few years the methodologies of near-field optics have been developing into defined procedures that allow for the general applicability of such techniques with their powerful potential to provide unique, new, super-resolution, optical instruments.

The method that is now universally used for preparing reproducible subwavelength optical elements for near-field optics was introduced by our laboratory [2]. In this method glass structures are pulled under microprocessor control with defined heat, tension and cooling. The smallest structure that we have pulled to date has an outer diameter of ~ 100 A. There is known to be a hole in this structure since water deposited in the large end of the pipette eventually trickles through this molecular dimension orifice. Based on the experience with somewhat larger structures we believe that the hole is on the order of 30 A.

The Research Goal

The goal of this research and the development program in this proposal was to use the molecular dimension orifice at the tip of the pipette as the vessel for a nanometer dimension light source and to apply this light source in unique ways to optical memory applications.

Achieving This Goal

Choosing the Near-field Optical Element

The approach of near-field optics that was applied in the original papers [1,2] was to transmit light through the reproducible subwavelength aperture that can be generated at the tip of a highly tapered glass structure. Although this methodology has worked marvellously to demonstrate the potential of near-field optics and is currently used in all laboratories that are beginning to practive near-field optics, it is not sufficient to achieve the ultimate resolution of the method, to achieve the maximal speed and to achieve the integration with far-field optical elements in order to generate usable devices for practical applications such as optical memories.

Light transmission through subwavelength apertures is limited by the rquirement that both the region of subwavelength transmission and the metallic coating surrounding this subwavelength region have to be minimized if applicable light intensities are to be achieved at the aperture. Because of these limitations the metal coated tapered glass structures have to be pulled with a sharp taper angle. With this requirement of sharp taper angles small apertures cannot be produced.

To achieve apertures with the dimensionalities of 30 A discussed above small taper angles are required and this results in exponentially decreasing intensities as the extent of the region of subwavelength transmission increases. The essence of this proposal is to overcome this limitation of near-field optics and to develop methods that generate light within the subwavelength aperture itself. This allows any taper angle to be used. In addition, as the tip is reduced in size the decrease in the signal is not exponential as is the case in transmitting light through a subwavelength aperture but is rather related to the change in the area of the emitting tip. Thus, this approach has the

potential of generating molecular dimension apertures that have the potential to produce applicable intensities of light.

To convert the subwavelength vessel of the nanopitte from an aperture into a light source we advance, in this proposal, the pipette technology by growing materials in the subwavelngth tip of the pipette that can be electrically excited to produce light at the surface of the nanoaperture. Our efforts focus on the pipette structure since this structure has been shown to be very sensitive to surface forces [3] and this sensitivity permits such glass structures to be reproducibly lowered into the near-field without adverse effects to the nanoaperture at the tip of this glass based force sensing element. In addition, the nanopipette tip can be bent [3] and this allows its effective integration into far-field geometrical optical elements. Furthermore, this bent structure is also applicable to rapid scanning methods that can be integrated into optical memories.

Specific Research Goals

Electroluminescent Polymer Growth

During the past year in coorperation with the Cavendish Laboratory at the University of Cambridge we have been able to form the electroluminescent polymer p-phenylene vinylene (PPV) [4] in the tip of a pipette with a 100 μ outer diameter. The inner diameter of this pipette was probably ~30 μ but this could not be measured as noted above. Inspite of this success the ability to make effective light sources with this polymer were limited since electron injection has proved difficult and the electrical to photon efficiencies were very low (< 1 %). Furthermore, the best efficiencies were only achieved with low work function electrodes such as calcium which were very susceptible to degradation. Such electrodes are not suitable for practical devices and are next to impossible to insert into the pipette.

In recent work this group has shown [5] that polymers can be generated that can use electrodes for injection with higher work functions, eg. aluminum. These metals are also less susceptible to degradation and exciting new methods of laser assisted deposition of these metal from vapors of metal organic compounds [6]. Such methods should yield the necessary metal electrodes in contact with these new electroluminescent polymers on the inside of the pipette. The external electrode is transparent and is formed from indium oxide. An important development with regard to these new electroluminescent polymer materials is the order of magnitude increase in their electrical to photon efficiency. Thus, both the development of the higher efficiencies and the capability of using higher work function stable electrodes gives us hope that we will succeed in generating light sources of a few nanometers in dimension.

The Growth of Semiconductor Based Light Sources in the Subwavelength Tip of a Nanopipette

Although electroluminescent polymers are the easiest to deposit in the nanometer dimension tip of the pipette, the semiconductor based device structures exhibit the highest electrical to photon efficiencies available today with the possibility of investigating structures that could support laser action.

During this grant period we have developed a unique procedure to grow such materials in the highly confined space of a pipette tip. In this procedure a quartz pipette is employed. It is filled with crushed GaAs and a carbon dioxide laser is scanned over the crystals. Materials grown by this unique method were intially characterized using an elemental analysis with the scanning electron microscope and with laser excited photoluminescence spectroscopy. From the chemical analysis we were able to determine that the gallium and arsenide stochiometry was appropriate. In addition, photoluminescence spectra were obtained at room temperature using an argon ion laser that illuminated the sample at 514 nm. In summary, the results we have obtained thus far indicate that the GaAs crystals grown in the tip of the pipette by our newly developed laser scanning growth technique are indeed of high quality.

A more sophisticated experimental arrangement replaces the borrowed carbon dioxide laser with a simple sealed tube laser and a colinear HeNe laser beam for better alignment. We also incorporated a scanning mirror assemby with the possiblility of impressing a ramp voltage to translate the laser beams along the axis of the nanopipette. In addition, an assembly rotates the pipette during the growth phase. Based on our previous experience we believe that better growth conditions will be achieved if we split the carbon dioxide laser into two beams. One of the beams will be used to heat the whole region of the pipette tip while a second beam will be passed through a lens and will be focussed to a small spot. This will allow the focused laser beam to be scanned along the region of the pipette tip while the whole end of the pipette is kept somewhat below the melting temperature of the semiconductor. As the semiconductor material is repeatedly melted by the focused laser beam on the pipette tip, the melt is drawn by the capillary action into the very tip of the nanopipette. This could be considered as a laser based modified Czochralski approach for crystal growth in confined media.

In general, crystal growth of any material in capillaries, e.g. nanopipettes, sets a challenge that has rarely been tackled even in basic research. Consider, for example, the growth in a 10 nm, or smaller, tip of a pipette. In such a structure we are dealing with solidification not only in an unusually confined space but also one with a high degree of curvature. Systems with highly curved surfaces considered until now include spherical nuclei in vapors undergoing condensation (positive curvature) and liquid condensing from the vapor (negative curvature). The scarcity of research in this field is explained by the small size of such systems containing what is commonly referred to as "less than a statistical number of atoms". The meaning of this phrase is that thermodynamics which deals with the average properties of large systems is not applicable in such cases. What

is really needed is a methodical treatment of the problem including the effect of curvature and this is indeed possible theoretically with the pipette providing a practical nanovessel to test our theoretical approaches.

To outline the theoretical basis for our ideas we consider first the solidification of a one-component system describing GaAs, InGaP or Si adequately. The rate of crystallization of liquids that are relatively fluid at their melting temperatures is usually fast and limited by the rate of removal of the heat of fusion. Nevertheless, liquids can often be supercooled well below their melting points, showing that in these cases the rate of liquid-crystal transformation is controlled by nucleation. The critical size for a solid particle nucleation in the liquid is given by the condition dG/dr=0, or the minimum of the Gibbs free energy of the system as a function of the radius of say a spherical particle.

For the simple case of such a spherical particle, the critical radius is given by

$$r^* = (2g_{sl}T_m)/(L_f DT) \qquad (1)$$

which can be directly obtained from the capillarity, or Gibbs-Thomson, equation. Here, g_{sl} is the solid/liquid interfacial energy, T_m is the material melting point, L_f is the latent heat of solidification and DT is the undercooling. Taking, for our case, $r^* = 5$ nm and the known GaAs physical parameters: $g_{sl} = 126$ erg/cm^2, L_f=262 cal/cm^3 and $T_m = 1510$K, we obtain DT = 70K.

The critical energy that the system must acquire for such nucleation is given by

$$DG^* = (16\pi g_{sl}T_m)/[3L_f(DT)/2], \qquad (2)$$

and for DT = 70K this is equal to approximately 80 kT. This is in good agreement with the average experimental nucleation energies of 78 kT measured for many metals. In calculating g for our curved surface we have taken into account the result obtained using statistical methods, namely $g_r/gv = (1+2d/r)^{-1}$, where d has the value of molecular dimensions. This gives a small correction to the calculated value above of the minimum undercooling. Also, larger nuclei at smaller undercoolings can be formed at the pipette tip. This would require larger critical energies for the case of homogeneous nucleation. However, the pipette walls serve as sites of heterogeneous nucleation allowing for the reduction of the potential energy for nucleation due to partial wetting of the silica by GaAs or InGaP. Success of the experimental crystal growth of GaAs described above proves the feasibility of our approach.

With this methodology of semiconductor growth in the nanovoid of the pipette tip we plan in the future to investigate structures in which the electrode in the inside of the pipette will be a gallium/indium eutectic which is a liquid at room temperature and can be easily introduced into the pipette. This inner electrode is also highly reflecting and could also be ideal as a highly reflecting mirror for a microlaser cavity. In fact the sturcture of the nanopipette is ideal for such a laser cavity. The tapered nanostructure at

one end also acts to reflect light. However, unlike the highly reflecting gallium/indium contact, the nano-orifice acts to allow partial transmission of the light at this orifice.

We hope to not only obtain nanolight sources and lasers with practical, high intensities but from a fundamental point of view these structures will also allow us to investigate the optical properties of both photon and exciton confinement in a wire of quantum dimensions both from an optical and electrical perspective.

Single Atomic and Molecular Resolution with Light

To achieve the ultimate in resolution and speed high intensity light sources of nanodimensions are not the only requirement. An important additional aspect of the research and development program was to investigate mechanisms of excitation that would be unique to the near-field methodologies we are focusing on in this proposal. One of these approaches is based on efficient, localized exciton generation which can be produced in the microcrystal probes described above. This raises the possibility of the ultimate in near-field optical excitation and resolution namely the transfer of an exciton from the tip to a surface which contains an acceptor for this exciton. Of additional significance would be the alteration of the optical properties of the acceptor by exciton transfer.

For such an approach the exciton filled nanopipette tip is scanned over a surface with appropriate acceptors whose excitation energy band overlaps the energy level of the donor excitons. Each time the crystal passes over an acceptor highly efficient energy transfer should occur and either subsequent emission or photochemistry will occur in the acceptor. For such efficient energy transfer the tip sample separation has to be on the order of the Forster radius which can be as large as 100 . The Forster radius is defined as the radius at which there is a probability of 50 % energy transfer. In other words, to excite a substrate by this uniquely near-field approach only two photons are required. With conventional excitation using freely propagating photons 10^9 photons are required to obtain a reasonable probability of excitation. Thus, exciton excitation has the potential of efficiencies of excitation that are orders of magnitude larger than with freely propagating photons.

The substrate that we are focusing on for such near-field optical memories is a unique membrane called the purple membrane. This is a distinctive crystalline membrane that grows in copius quantities. It is the only crystalline membrane found in nature. It grows in the bacterium, *Halobacterium halobium*, that is found in the Dead Sea. The membrane is composed of a single molecule which is similar to the pigment in our eyes, rhodopsin, that senses light. This pigment is called bacteriorhodopsin. Plastic films made of this membrane are of ultrahigh optical resolution < 0.1 m [7]. This probably occurs because the individual pigment molecules are excitonically uncoupled due to the polymer that surrounds the small, polyene molecule in the protein that absorbs the light. This polyene component is also an excellent acceptor of excitons and the wavelength at which it can accept these excitons can be readily tuned. Recently, we

have discovered that the molecules, which can be switched between two stable states with light, also exhibit different charge properties. Thus, one of the goals of this research is to excitonically switch the absorption of this pigment with light and to sense this switch by monitoring the changes, non-destructively using the Coulombic force between the tip and the surface. The indefinite thermal stability of the two states and the reproducibity of the effects in this membrane over at least the10^7 cycles that we have investigated in our laboratory [8] with conventional optical excitation gives us hope that this combination of near-field exciton excitation and non-destrctive read-out will result in the revolution that will be required in order to dislodge the established far-field techniques in vogue today. The demands of the avalanche of information storage and retrival is such that revolutions will be required.

New Methods of Nanopipette Fabrication

The nanopipette light source is also an exquisite force sensor [3]. For highest sensitivities techniques are being developed to bend the electroluminescent tip of the pipette so this near-field element can be used for write/erase and non-destructive read operations.

To produce such cantilever pipette structures reproducibly and with the highest resolution a carbon dioxide laser will be used to bend the glass and quartz micropipettes instead of the flame that has been used until now. By focusing the beam of the CO_2 laser down to a few tens of microns and passing the pipette through the focus with a micromanipulator, sharp, clean and very reproducible bends of less than 50 m from the tip should be able to be produced. Both the position and the angle of the bend should be controllable by adjusting the size of the focal spot and the speed at which the tip is passed through the beam. The micropipette should remain hollow as the tip is bent just as it remains open during the initial pulling of the nanopipette. The heating is very localized and should not effect the actual tip dimensions. The resulting nanopipette force probes should be sharper, stronger and have a higher aspect ratios than any other atomic force microscopy probes available today.

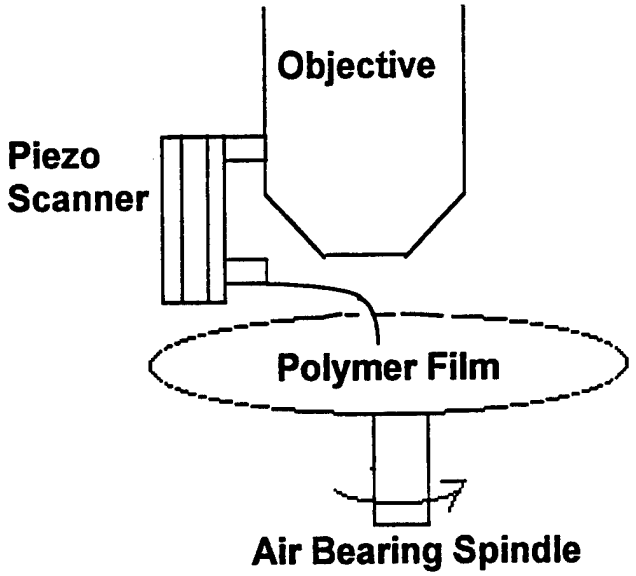
A second important direction in pipette facbrication is to resolve the problem of attaching a micro-mirror to the bent structure as has been accomplished in the past. Such mirrors are essential so that the simple technology of position sensitive force sensing can be used to detect the cantilever motion that monitors the Coulombic repulsion with high sensitivity. For high reproducibility and automation of the operation we plan to use standard pipette polishing methodologies to generate a flat reflecting surface integrated directly into the structure of the pipette probe. There will be no additional mass as was the case with the micro-mirror so the resonance frequency and Q factor of the probe are much improved. The pipette can then be coated with a thin film of aluminum to further enhance the reflectivity of the surface if desired. This surface should be ideal for cantilever deflection sensing of by a focused laser beam which can be reflected off the polished surface onto a position sensitive detector. In addition to position sensitive detection techniques fiber and other interferometric techniques will also be compared for

their sensitivity and speed of response and the most appropriate methodology will be incorporated into the optical memory device we are designing.

Rapid Scanning of an Integrated Near-field and Far-field Optical Element

A final element that was the focus of the research and development program was the requirement to effectively integrate the near-field element into a standard lens that views in the far-field an overlapping field of view. This is crucial for rapid random access. Thus we have built a piezoelectric collar for standard lenses used in optical disc systems. To this collar will be attached the bent pipette. A small section of the field of view will be obscured by this arrangement but we do not anticipate any serious difficulty in obtaining infomation on the disc area containing the information at standard optical resolutions. This allows the rapid viewing of the entire disc in order to place the pipette tip over the region of the disc that contains the information requested. At that point the tip lowered to the surface with force sensing in order to write, erase or read a written field with nanometer resolution.

For rapid scanning we intend to incorporate the far-field near-field optical element into an assembly that will have a stage that will spin under the pipette. The spinning stage will be driven by air bearings and the polymer medium will rest on the spindle driven with air bearings as is seen below.



This should permit us to achieve large linear velocities of 10-3000 mm/sec and high data rates. Based on the considerable experience that we have in generating nanopipette structures we estimate that the spring constant and the resonance frequencies will allow writing speeds of at least 500 kHz with this arrangement. Even in contact we expect little wear since we have completed test experiments with the pipette in contact with loads of even 10^{-5} N and we have not seen any loss of the surface charge that is tightly bound to the individual molecules that have been illuminated in the polymer film. We

will vary various aspects of this arrangement including the mass, the geometry, the resonant frequency and the applied load. We expect that the considerable flexibility of this approach should allow the combination of super-resolution with high data rates to be achievable.

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